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# Synthesis, crystal structures and luminescent properties of the copper(I) pyrazolonate complexes

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ABSTRACT

New copper(I) complexes with pyrazolonate ligands [Cu(Pr$^i$-PMP)(DPEphos)] (**1**) and [Cu(Bu$^t$-PMP)(DPEphos)] (**2**) (Pr$^i$-PMP = 1-phenyl-3-methyl-4-isobutyryl-5-pyrazolonato, Bu$^t$-PMP = 1-phenyl-3-methyl-(2,2-dimethylpropan-1-oyl)-5-pyrazolonato; DPEphos = bis[2-(diphenylphosphino)-pheny]ether) were synthesized and structurally characterized. An unusual $\eta^1$ cocoordination of pyrazolonate ligand to the copper atom was found in complex **2**. Photo- and electroluminescent properties of the synthesized compounds were investigated. In crystalline form compounds **1** and **2** revealed dual emission consisting of the bands at 445–450 and 485–488 nm which were assigned to transitions from the $S_1$ and $T_1$ states. DFT and TD DFT calculations as well as electrochemical studies correlate with the photophysical data. Synthesized copper(I) complexes generated electroluminescence of yellowish-orange (**1**) and yellow (**2**) colors with the maximum luminance of 286 and 39 cd/m$^2$, respectively.



## 1. Introduction

In the current decade there has been a growing interest in electroluminescent copper(I) complexes [1–15]. Although the copper-containing emitters are still inferior by efficiency to well-known phosphors based on cyclometalated iridium(III) and platinum(II) complexes [16,17], their application for OLED devices fabrication is very attractive. In comparison with iridium and platinum compounds, copper(I) complexes are relatively abundant, inexpensive, and non-toxic. Therefore the development of new efficient copper(I) emitters is an urgent problem.

The most of electroluminescent copper(I) compounds are ionic complexes which consist of $Cu^+$ bonded to diimine and phosphine ligands and the $[BF_4]^-$ or $[PF_6]^-$ anions [2–10]. As a rule, such compounds revealed moderate thermostability and low volatility. These unfavorable properties restrict essentially the possibility of preparation of the emitting layers from ionic copper(I) complexes by vacuum deposition. For this reason the emitting layers were fabricated by spin-coating using solutions of such copper(I) compounds.

Recently neutral electroluminescent copper(I) complexes were synthesized and applied for fabrication of emitting layers in OLEDs by the vacuum deposition technique [11–15]. The air stable and volatile neutral complexes of copper(I) with the phosphine and 4-acyl-pyrazolonato ligands are known [18], however, their luminescent properties have not been investigated. It should be noted that cyclometalated iridium(III) and platinum(II) compounds with pyrazolonate ancillary ligands were found to reveale efficient electroluminescent (EL) properties [19–22]. These findings stimulated us to explore luminescent ability of copper(I) pyrazolonate derivatives. The published data allowed to expect copper(I) pyrazolonate derivatives to be efficient luminophores as well.

Herein we report the synthesis, characterization, photophysical and EL properties of the new neutral copper(I) complexes **1** and **2** with pyrazolonate and phosphine ligands.

## 2. Experimental

### 2.1. Materials and physical measurements

All manipulations were carried out in evacuated sealed ampoules or in argon using standard Schlenk techniques. The

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